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SULPHURIC ACID MANUFACTURE.

BY

HENRY ARTHUR SMITH.

THE CHEMISTRY

OF

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To Dr. R. ANGUS SMITH, F.R.S.

My dear Uncle,

To no one can I dedicate this small volume more fitly than to you, to whose never-varying kindness and ever-ready help I ascribe whatever of scientific worth it may contain.

The contents have, as you know, been published to some extent before; but it was thought that it would be useful to those engaged in sulphuric acid manufacture if the results were to be brought together in a more compact form. Hence this little book.

It was not considered necessary to supply it with an index, as the headings of the various chapters sufficiently indicate the matter contained in them. The great aim has been to make it as quiet and as unpretending as possible.

Ever, my dear uncle,

Yours very sincerely,

H. A. SMITH.

Manchester, *May* 1873.

INTRODUCTION.

SULPHURIC ACID has been known from very early times; although we cannot with certainty assign any date to its discovery, it appears probable that it was discovered in the year 806 by Rhazes, a physician in Bagdad, and not, as has been often affirmed, by Basil Valentine. This point, however, must be left to others more competent than myself to judge of it. One thing, however, seems certain, that it was first prepared by the distillation of sulphate of iron—green vitriol. This substance, when submitted to a high temperature, yields a mixture of sulphuric and sulphurous acids, the sulphuric acid thus obtained receiving the name of "Nordhausen sulphuric acid," from the name of the place where, at the present day, this manufacture is still conducted by the distillation of the sulphate of iron.

As time wore on, however, and other manufactures became more extensive, this acid was required in much larger quantities and on a less expensive scale. It is to

Dr. Roebuck, of Birmingham, that we owe the method at present employed, and which, since its introduction, has undergone comparatively little change. The changes that have been made have principally tended towards the removal of practical difficulties, whilst the principle involved in the original process remains the same.

Sulphuric acid manufacture, as carried on at the present day, may be divided into three parts:—

1. Burning sulphur or a sulphur ore in furnaces, or, as they are technically called, "kilns." (Figs. I., II., III.)

2. A large chamber in which the condensation of the acid takes place, formed of sheets of lead.

3. The necessary supply of air, of gaseous nitric acid and steam.

When sulphur is ignited in a current of air it volatilizes, and, robbing the air of part of its oxygen, becomes converted into sulphurous acid (SO_2). This sulphurous acid, which, in its original condition, is in the form of gas, passes from the kilns by means of a flue, enters the lead chamber (No. 2 above), where, on coming in contact with the gaseous nitric acid and steam, it becomes converted into sulphuric acid at the expense of part of the oxygen of the nitric acid gas, which becomes converted into nitric oxide; this, in its turn, seizes the oxygen present in the air, and returns to its original condition.

This, as may be seen from the description, is a *continuous process.* And theoretically, although we find

not so practically, a small amount of nitric acid is able to convert an unlimited amount of sulphurous acid into sulphuric acid, whilst the steam which is present in the chamber merely acts as a carrier of oxygen from the air to the nitric oxide.

The lead chamber, in which the condensation takes place, is built of numerous separate sheets of lead, soldered together at the edges by means of the hot flame of burning hydrogen, thus omitting the use of any substance which would be liable to be acted upon by the chamber gases, or by the acid itself. This large continuous chamber is generally about 100 feet long by 20 feet high and 30 wide. The size, however, depends entirely upon the views of the manufacturer.

This, then, is the rationale of sulphuric acid manufacture, seemingly a simple and straightforward process enough, but one which in reality requires very great care and attention. The great difficulty with which manufacturers have to deal is the proper management of the lead chamber, and the object of the present work is to endeavour to show the conditions under which the greatest amount of action between the chamber gases can take place, and to lay down certain definite rules for workmen to follow, instead of trusting to the general "rule of thumb" management of the present day. Although this rough method may not be done away with all at once, yet I trust the following inquiry will lead an intelligent manager or foreman to trace to their cause, in a much surer and more rapid manner,

the ills to which the chamber under his charge is subject.

Having been for some time connected with this manufacture, I greatly felt the want of some such guide, and commenced a series of investigations into the various conditions of the occurring actions among the gases—their combinations and permutations, and the laws to which they are subject. The result of these investigations I here lay before the public.

In the following pages I shall deal with sulphuric acid made from pyrites (sulphur ore), as in this is naturally included that made from pure sulphur; but the former was chosen, as it forms a great stumbling-block to manufacturers on account of the impurities it contains, and the difficulty of removal which these impurities present.

[Fig. 1.

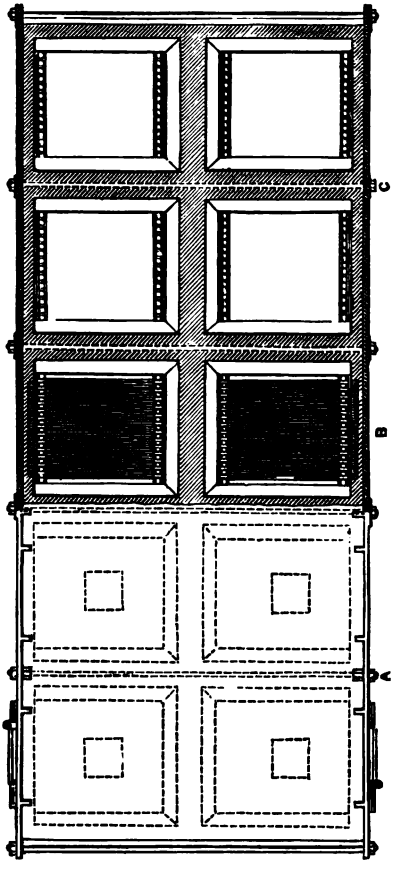

Fig. 1.

FIG. 1.

View of a set of ten kilns for burning sulphur ores.

Ground Plan.

Here the kilns are placed back to back, and take up less room than when each is built separately.

B. shows the grates upon which the ore is thrown.

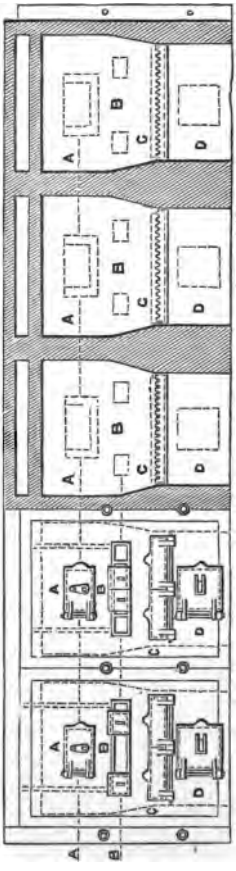

Fig. 2.

FIG. 2.

Section of pyrites furnace.

A. Charging door.
B. Door by which the charge is stirred and changed.
C. Movable grate.
D. Door by which charge is withdrawn.

Fig. 3.

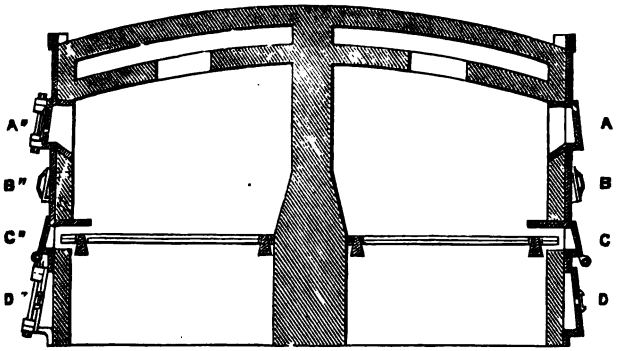

FIG. 3.

Front of the pyrites kilns.

A. Charging door.

B. Door by which the charge is stirred and changed.

C. End of movable grate. In No. 2 the bars of grate are shown: in No. 3 the rests for bars.

D. Door by which charge is withdrawn.

THE CHEMISTRY

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SULPHURIC ACID MANUFACTURE.

On the Presence of Arsenic.

THE great drawback in the manufacture of sulphuric acid from pyrites is most undoubtedly the presence of arsenic. Its removal, even if it can be done completely, is a work of difficulty and expense, as in our methods for purification we must take into account the various uses to which the acid is to be put. It is my intention in the present chapter to trace this impurity (arsenic) from the original pyrites, through the various operations with which the acid made from it is connected, to the last stages of alkali-manufacture; and to show also that, not content with throwing the injurious gases of sulphurous and hydrochloric acids into the air, alkali-works must bear the blame of polluting the atmosphere with the still more dangerous substance —arsenious acid. Although the amount escaping from a single work is comparatively small, yet, when we consider the number of works using pyrites in the for-

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mation of sulphuric acid, we must confess that in the end it mounts up to something very considerable.

General amounts in various pyrites.—There are two things to be looked to in choosing an ore for sulphuric acid manufacture. 1st. Its breaking property, if I might so call it, that is, its power of breaking into small lumps without leaving what are technically called "smalls." 2ndly. Its freedom from arsenic.

If we compare the amount of arsenic in published analyses of various kinds of pyrites, we shall be astonished at the difference between these and the amounts of arsenic found in the acid manufactured from the same ores. From ores containing from 0·21 to 0·31 per cent. arsenic we have acid containing from 1 to 1·5 per cent. arsenic.

Taking, for instance, the analyses of various pyrites given in Richardson and Watts's 'Chemical Technology,' I find that the largest mean percentage of arsenic present varies from 0·31 to 0·33 per cent. arsenic, whilst some are mentioned as containing merely a "trace," and others as being perfectly pure—results, however, which are never corroborated when these ores are being worked on a manufacturing scale.

Being obliged, in my capacity as chemist in an alkali-work, to turn my attention to this subject, I determined to make an extended series of analyses of such specimens of pyrites as were likely to suit our purpose, and accordingly drew up a Table of results, which differed to a very great degree from those gene-

rally given. In the following Table, I give in Part I. the amounts of arsenic in the various ores given in Richardson and Watts's 'Chemical Technology;' and in Part II. my own analyses are given at full length. The differences are very great; still I remain satisfied of the truth of my own results when I consider that the increase in the different specimens obtained by laboratory analysis was an index to the increase obtained as the result of manufacture.

It will be proper to speak here of the best method for the determination of arsenic in pyrites. After much experience I have come to the conclusion that *fusion* is the most exact; oxidation with nitric acid not being so reliable. The method employed in the preceding analyses was as follows:—

A weighed quantity of the ore was fused with three parts of pure carbonates of soda and potash, and one part pure nitrate of potash, for about ten minutes. The addition of chloride of sodium was, I found, perfectly unnecessary for the estimation of the arsenic. The residue was then boiled well with water and filtered; the insoluble portion was again treated in the same manner, and the filtrate from it added to that of the former. This filtrate was carefully evaporated to one quarter of its bulk, and the arsenic determined by two separate methods—1st, by precipitation as tersulphide of arsenic; and, 2ndly, as the arseniate of ammonia and magnesia, *both dried on a weighed filter.**

* Some prefer dissolving the precipitated tersulphide of arsenic, and

It is absolutely necessary in every case to fuse the residue remaining from the first fusion, as in most cases this contains the greatest amount of arsenic.

The methods of analysis of the products obtained from the sulphuric acid were simply modifications of this process, unnecessary portions being omitted.

TABLE I.

PART I.	
Name of Pyrites.	Arsenic per cent. Mean.
Spanish	0·21 to 0·31
Belgian	trace
Westphalian	trace
Norwegian	none
Irish*	0·33
Cornish	0·32
Italian	trace
Swedish	trace
Cleveland..	——

then reprecipitating as arseniate of ammonia and magnesia. The results, however, obtained by the latter process are invariably too high.

* In Table I., Part I., the largest amount of arsenic present in any ore is in the Irish, and even then the amount is comparatively trifling. In some Irish ores that have come under my notice the result has been very different from that given in the Table. I have analysed ores containing 2 per cent. and even 2·3 per cent. arsenic, and one of our most successful acid manufacturers assures me that he has often had Irish ores containing even a larger percentage than that which I have given.

TABLE I.—*continued.*

PART II.		
	Arsenic per cent.	Mean.
Spanish :—		
Tharsis' .	1·542, 1·620, 1·644, 1·790, 1·526, 1·700, 1·552, 1·661, 1·686, 1·796	1·651
Mason's .	1·744, 1·810, 1·891, 1·770, 1·661, 1·692, 1·711, 1·754, 1·601, 1·719	1·745
Belgian . .	1·000, 0·664, 1·621, 0·743, 1·002, 0·624, 0·972, 0·924	0·943
Westphalian	1·886, 1·794, 1·802, 1·936, 1·899, 1·900, 1·921, 1·889	1·878
Norwegian :—		
Hard . .	1·440, 1·916, 1·633, 1·621, 1·648, 1·611, 1·692, 1·631	1·649
Soft . .	1·794, 1·731, 1·664, 1·632, 1·700, 1·621, 1·816, 1·709	1·708

Here the Belgian pyrites contains the smallest amount of impurity; but this had the fault, on being broken, of crumbling very much and leaving a large amount of "smalls." The next in order of purity is the hard Norwegian. This was a good breaking and burning ore, firm, compact, and easily raised to a red heat in the kilns; so it was found preferable to burn this ore, even with the increased amount of impurity, rather than use the Belgian containing a small amount, but which carried along with it the great inconvenience of making "smalls."

Arsenic present after burning.—After the hard Norwegian pyrites has been burnt, I find a trace of arsenic still remaining in the burnt ore; this amount is very small—four analyses giving as an average only 0·465 per cent., so that the greatest amount of that originally present has been expelled from the pyrites.

Deposit in flue leading from kilns to lead chamber.—This flue when cleaned out presented a strange appearance. Its length was about twenty feet, and, with the exception of about ten feet from the "kiln" end, was thickly coated (and even partially filled) with a shining deposit, which on examination proved to be a mass of sulphur in a perfectly viscous state, containing 46·360 per cent. arsenic trioxide.

When lighted it burned with the ordinary blue sulphur-flame, and on inserting a piece of cold porcelain in the vapour, gave a deposit of sulphur along with a considerable amount of arsenious acid. (See Table II.)

Sulphuric Acid.—Passing along the flue into the chamber, I find the sulphuric acid containing a large amount of arsenic. As an average of twelve analyses, 1·051 per cent. arsenious trioxide is the result; so that in passing through the flue above mentioned it must have lost a large proportion of that originally present in the pyrites. (See Table II.) It is from the sulphuric acid itself that the arsenic should be removed, as this acid is the groundwork of the whole following alkali-manufacture.

Deposit on bottom of lead chamber.—On the bottom of the lead chamber, and sometimes on the sides, a grey siliceous mass is found, interspersed here and there with clusters of delicate regular crystals, the transparent elongated prisms of arsenic acid. The transformation from the arsenious acid we find in the flue to the arsenic acid of these crystals, has evidently been completed

along with the oxidation of the sulphurous acid. In this deposit the percentage of arsenic trioxide varied from 1·811 to 1·9 per cent., the rest consisting of sulphate of lead and silica. (See Table II.)

Hydrochloric Acid.—When the sulphuric acid made from pyrites is mixed with common salt in the reverberatory furnace for the formation of sodium sulphate, the arsenious acid present in the acid is converted into the terchloride of arsenic, and escapes along with the hydrochloric acid to the condensing-towers. This conversion is very nearly complete, as the amount of arsenic present in the sodium sulphate is very small. In the hydrochloric acid a mean of eight analyses gives 0·69 per cent. arsenic trioxide, the amounts varying from 0·589 to 0·911 per cent. (See Table II.)

Sulphate of Soda.—The amount present in this is very small. As mentioned above, the conversion from the teroxide to the terchloride of arsenic is wonderfully complete, the percentage in the sodium sulphate being only 0·029 per cent. (See Table II.)

This still shows us how careful we ought to be in obtaining pure sulphate of soda for medicinal purposes.

Table II.

Substances in which arsenic is present.	Arsenic (trioxide) per cent.															Mean.
Pyrites (hard Norwegian):— Before burning	1·440	1·916	1·633	1·621	1·648	1·611	1·692	1·631	..	..	..	..	..	..	..	1·649
After burning	0·562	0·356	0·469	0·454	..	..	..	..	..	..	..	..	..	..	..	0·465
Sulphuric acid	1·112	1·026	1·051	1·190	1·141	0·991	0·861	1·036	1·100	1·420	1·003	1·032	0·800	1·006	0·999	1·051
Deposit in flue leading from pyrites-kilns to lead chamber	46·499	46·431	45·911	46·600	..	..	..	..	..	..	..	..	..	..	..	46·360
Deposit on bottom of lead chamber	1·861	1·900	1·811	1·825	1·890	..	..	..	..	..	..	..	..	..	..	1·857
Hydrochloric acid	0·711	0·642	0·686	0·599	0·700	0·693	0·589	0·911	..	..	..	..	..	..	..	0·691
Sulphate of soda	0·006	0·044	0·050	0·032	0·024	0·020	0·023	0·021	0·033	0·045	0·009	..	0·060	0·081	..	0·029
Soda-waste	0·611	0·222	0·190	0·462	0·527	0·643	..	..	..	..	..	..	..	..	..	0·442
Carbonate of soda	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Recovered sulphur:— Mond's process	0·901	0·842	0·616	0·442	..	..	..	..	..	..	..	..	..	..	..	0·700
After purification	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—

TABLE III.

Tons.		Ton As.
100	Hard Norwegian pyrites (Table I.) contain, before burning .	1·649
"	" " " " after burning .	0·465
	tons.	
100	Hard Norwegian pyrites make 140·875 H^2SO^4, containing .	1·481
140·875	Sulphuric acid make . . . 104·9 HCl " .	0·724
"	" " 204·12 Na^2SO^4 " .	0·059

In this Table the amounts are given in a manner more useful to manufacturers.

Deposit in flue leading from salt-cake furnace to condensing-towers.—This flue, about twenty feet long, leads, for the most part in the open air, from the salt-cake furnace to the condensing-towers. The part from which the deposit was taken was about fifteen feet from the furnace. At first sight the deposit seemed to be composed merely of common salt and a little sodium sul·

TABLE IV.

Flue from Salt-cake Furnace to Towers.—Deposit.

No. of analysis.	Arsenic trioxide.
	per cent.
1.	44·664
2.	42·936
3.	45·333
4.	39·982
5.	46·449
6.	44·398
7.	40·441
8.	38·977
9.	47·732
	390·912
Mean . . .	43·4346

phate, but on examination with a hand-microscope small octahedral crystals of $As^2 O^3$ were distinctly seen.

On analysis this deposit gave 43·4 per cent. arsenic trioxide. This flue had been in constant use for some years. (See Table IV.)

Coke in condensing-towers.—Although not expecting to find any arsenic in this, thinking that the water in the towers would completely decompose the chloride of arsenic which escaped from the reverberatory furnace, I made an analysis for it. For every analysis 10 lbs. of coke were employed, and digested first with pure distilled water and afterwards with perfectly pure hydrochloric acid. Arsenic was very easily detected in this solution. As an average of three analyses, I find 2·8 per cent. arsenic trioxide, the variation being from 2·6 per cent. to 3·2 per cent. $As^2 O^3$. It is difficult to imagine how this arsenic has been retained in the coke, as it would have been expected that the decomposition of the terchloride by the water in the towers would have been complete. (See Table V.)

TABLE V.

Coke from Condensing-towers.

No. of analysis.	Arsenic trioxide.
	per cent.
1.	2·641
2.	3·182
3.	2·837
	8·660
Mean . . .	2·886

Air in flue from condensing-towers to chimney.—Not only is the decomposition of the arsenic terchloride not completed in the towers, but a considerable amount of arsenic (in what condition I am not aware) escapes from the flue leading from the condensing-towers to the chimney of the works. The amount of air passing through this flue was 31,722 cubic feet per hour, and for each analysis 500 cubic feet were taken. The method employed for collecting the arsenic (trioxide?) contained in the air passing through this and the next-mentioned flue was as follows:—The air was aspirated through three bottles containing respectively H^2O, HCl, and $AgNO^3$. The gas was allowed to bubble very slowly through the solutions; the bottles containing them were capable of holding 40 ounces, and were about half filled. It was found in most cases (it might almost be said in *all*) that the $AgNO^3$ solution was unnecessary, the H^2O and the HCl absorbing all the arsenic which was in the air drawn through.

As an average of twelve analyses, the following results were obtained:—

$As^2 O^3$ per 1000 cubic feet.	$As^2 O^3$ per hour.	$As^2 O^3$ per day.
0·158 grain.	5·012 grains.	120·282 grains.

This amount may appear small; but when we consider that the 120 grains per day are from the chimney of one works only, the question becomes rather a serious one when we take into account the number of manufactories employed daily in throwing this amount into the

air even within a short distance of Manchester. (See Table VI.)

TABLE VI.

Flue leading from Condensing-towers to Chimney.
Amount of air taken for each analysis = 500 cubic feet.
Amount of air passing = 31,722 cubic feet per hour.

No. of analysis.	$As^2 O^3$ per 1000 cubic feet.	Amount per hour.	Amount per day.
	grain.	grains.	grains.
1.	0·068	2·157	51·768
2.	—	—	—
3.	0·082	2·601	62·424
4.	0·072	2·284	54·816
5.	0·102	3·235	77·640
6.	0·064	2·030	48·720
7.	0·198	6·280	150·720
8.	0·248	7·867	188·808
9.	0·186	5·900	141·600
10.	0·232	7·359	176·616
11.	0·262	8·311	199·464
12.	0·382	12·117	290·808
	1·896	60·141	1443·384
Mean . .	0·158	5·012	120·282

Closely connected with this is the specimen of

Air taken 10 *feet from bottom of chimney.*—The same amount of air was taken for each analysis in this case as in the former, namely 500 cubic feet, the mean of nine analyses in this case being

$As^2 O^3$
per 1000 cubic feet.
0·086 grain,

or nearly $\frac{1}{10}$ gr. per 1000 cubic feet. Surely such a state

of things ought to be prohibited. The arsenious acid thrown into the atmosphere must in some places be very large. Of its danger there can be no doubt. But the great problem will be how to prevent its escape. It is owing to no carelessness on the part of the manufacturers; and it is one of those things that in our present state of knowledge it is scarcely profitable to remove. On whom must the blame rest?

TABLE VII.

Specimen of Air taken 10 feet from the bottom of Chimney.

Amount of air taken for each analysis = 500 cubic feet.

No. of analysis.	$As^2 O^3$ per 1000 cubic feet.
	grain.
1.	0·046
2.	0·022
3.	0·086
4.	0·062
5.	0·112
6.	0·054
7.	0·122
8.	0·132
9.	0·144
	0·780
Mean . .	0·086

I hope to speak in another chapter on some of the methods employed for the removal of this "nuisance"; in the mean time I must proceed to speak of the

remaining substances of alkali-manufacture. The last examined was the sodium sulphate; the next to undergo analysis was

Sodium Carbonate.—This, up to the present time, has been found perfectly free from arsenical impurity; fifteen samples from twelve different works were submitted to analysis, and none was discovered.

Soda-waste.—In this the amount is comparatively trifling, giving as an average of six analyses 0·442 per cent. arsenic trioxide. (See Table II.)

Recovered Sulphur. Mond's process, before and after purification.—In specimens of sulphur recovered by Mond's process I have sometimes found great differences, the amounts varying sometimes from 0·442 to 0·901 per cent. arsenic trioxide; but its presence to this extent is only found in the unpurified samples. In those which have undergone purification none whatever is found, the average of four analyses of the unpurified sulphur being 0·7 per cent.

I think the foregoing analyses allow a simple and direct deduction to be drawn; and that is, if the arsenic is to be removed at all, everything points to the sulphuric-acid stage as that in which the removal ought to take place. Sulphuric acid is the corner-stone of alkali-manufacture; cleanse it, and the whole is clean.

Methods for Removal of Arsenic.

Two precautions have to be taken into account in the methods employed for the removal of arsenic from sulphuric acid.

1st. The substance or agent which is used in the purifying process must have no deleterious effect on any article in the manufacture of which the acid is required.

2ndly. We must prevent our works, as far as in us lies, from becoming a nuisance to our neighbours.

The item of expense is naturally a matter of course.

The following purifying agents have been carefully tried, with the following results:—

Sulphuretted Hydrogen in a gaseous state.—This is, I believe, in use in many cases, but, as far as I can make out, with very variable results. For my own part, I found it infringed the second requisite of a purifier, inasmuch as it became a "nuisance," and, which was much more serious, was too expensive. The plan employed in this case was a very simple one.

A leaden pan, three feet in depth and width, and twenty-four feet long, was nearly filled with the acid to be purified; into this pan sulphuretted hydrogen was passed by means of an iron pipe terminating in a leaden one where it dipped into the acid; this leaden pipe, which extended along the length of the pan, was drilled throughout its length with fine holes, through which the gas bubbled into the acid. After the arsenic had been all precipitated, the acid was run into another smaller pan of about one foot square, filled with fine coke, which rested upon a false drilled bottom; through this coke the acid filtered whilst the precipitated sulphide of arsenic was retained on the filter. This small filter was cleared out every day.

The leaden pan in which the precipitation took place was covered with a wooden roof having a small outlet leading into an iron pipe, which, passing out of the shed, was raised to a red heat, thus decomposing the escaping sulphuretted hydrogen. The sulphur thus obtained was then burned in the sulphur-kilns. The remaining gases were then passed into the chimney.

Whether from defective draught, or from the unsuitability of the process to the required purpose, this plan did not answer; whilst the use of acid to liberate the gas, together with the difficulty in regulating the supply, made the expense of working too great.

Instead of using separate acid to liberate the sulphuretted hydrogen, I tried to use that which was to undergo purification, by the addition first of

Sulphide of Iron.—The sulphide of iron was simply ground to a rather fine powder, and then added to the acid. This plan is, of course, only admissible in certain cases. For acid employed in wire-working, galvanizing, or similar work, purification by the simple addition of ground sulphide of iron is quite safe, and completely answers the purpose required; whereas that containing arsenic cannot be used, its action having a deleterious effect upon the iron. Acid purified by this means, however, cannot be used in bleaching, dyeing, or printing; so that its field of usefulness is extremely limited; still, as a purifying agent, it was all that was required.

Sodium Sulphide.—As this was a substance capable of being used in most cases, more care was expended on it than on either of the former. The sulphide of sodium employed was made from black ash, and, although contaminated with a little lime, answered the purpose completely. The method of application was as follows:—

A known amount of sulphuric acid containing a determined percentage of arsenic trioxide was run into a large leaden pan, and a calculated amount of sodium sulphide added. At the bottom of this pan a layer of coke, which had previously been well digested with hydrochloric acid to free it from iron and other impurities, was placed, through which the acid, being run upon it, filtered, thus freeing it from the precipitated tersulphide, whilst it was run out from the pan by a tap at the bottom. The precipitate was removed from this filter every night; but the coke was allowed to

remain for a long time, two or three months sometimes elapsing before removal. The escaping sulphuretted hydrogen was conveyed away by a process similar to that employed in the sulphuretted-hydrogen method.

The results obtained by this method were very satisfactory, and the expense was extremely moderate—one hundred gallons of sulphuric acid giving only a very minute trace of arsenic after being subjected to this process.

The deduction I naturally draw from the results of the above methods of purification is, that sulphuretted hydrogen can precipitate the last traces of arsenic in the acid it is required to purify. The only difficulty lies in the method to be employed, and the means of getting rid of the escaping sulphuretted hydrogen which has been allowed to be present in excess. It is necessary to state that the above method of decomposition of that gas did not fully answer the purpose required.

Sodium Chloride.—The next plan tried was purification by the addition of common salt to the acid. It was thus supposed that, according to the general rule, the arsenious acid would be converted into the terchloride of arsenic, and escape as such. This, however, was found unsuitable, for many reasons.

In the first place, the decomposition of the salt is not perfect, a considerable amount remaining in the acid as sodium chloride. Next, its action upon the ordinary brown vitriol (as it runs from the chamber) was found not to be so perfect as upon that undergoing

refining, so that it was necessary to add the salt to the glass retorts after they had been in action for some time. This, of course, entails great inconvenience. The necessity for opening the retort after the acid has been for some time in a state of ebullition is at once very disagreeable and very dangerous, whilst the sudden and powerful (partial) action upon the salt makes it an attempt not to be incautiously determined upon. If, on the other hand, the salt is introduced into the retort before the acid has commenced boiling, it collects in considerable amount at the bottom, and thus causes the mortality among the retorts to become a matter of some consideration, as well as making it a dangerous occupation for the man whose business it is to watch them, as the bursting of such a retort over a fire carries with it great danger. This plan then was thrown aside. Although it could compete with any in cheapness, yet it carried too many inconveniences with it to become practicable. The following numbers may perhaps be interesting:—

Sulphuric Acid. As $^{3}O^{3}$ per cent. (before purification).		Sulphuric Acid. As $^{3}O^{3}$ per cent. (after purification).
1·131	contained	0·34
1·303	,,	0·48
0·991	,,	0·63

The above figures show that the decomposition was not perfect enough for the plan to be made use of on a manufacturing scale. I had found it to answer perfectly in my laboratory experiments, and so hoped that,

when extended to the working scale, it would be equally successful.

Hydrochloric Acid.—A stream of hydrochloric acid gas was passed into the acid required to be purified, supposing the decomposition in this case would be similar to the above. This, however, was open to the same objections as the former, with the additional one that the expense entailed by the process is too great for any practical purpose.

In looking over the foregoing processes, one or two natural conclusions force themselves upon me. The process which, as far as I can yet see, we must rely upon for the purification of our acid is that which depends upon the use of sulphuretted hydrogen. Precipitation is much surer, and, indeed, more perfect, than decomposition. The latter is dependent upon too many conditions. The heat, the completeness of decomposition of the salt, the rapidity with which the liberated bubbles of hydrochloric acid gas pass through the acid, all exercise a great influence upon the success of the process. Whilst sufficiency of gas is the only requisite in the former case, the latter depends upon too many causes, too many conditions. Certainty in this case must be striven for before rapidity: once gain the former, and we may be sure of the latter following in its own good time. Besides, in the present condition of the law of the country in such matters, sulphuretted hydrogen is a much safer gas to throw into the atmosphere than hydrochloric acid!

I have thus given my own experience of the best methods of the purification of sulphuric acid, gathered during a pretty continued search after some sure and practical method both in respect of efficiency and economy. I have chosen to do this rather than gather together the experiences of others—partly because these experiences are comparatively few and far between, and partly because this matter has been looked upon by manufacturers as being of a merely secondary nature. But I was led to inquire into it in a more serious manner from the fact of having seen much acid returned to the manufacturers as being unfit for use owing to the presence (supposed!) of Iron, whilst all the disturbance arose from the presence of this extremely difficult-to-be-got-rid-of substance, arsenic. In several instances, also, which have come under my notice in the cases of manufacturers of ammonium sulphate, many hundred pounds' worth of material has been lost through the use of acid containing this impurity, while the unfortunate makers were vainly searching for their old enemy, Iron.

The importance of examination for the presence of arsenic can scarcely be too strongly urged upon the manufacturers of such materials. In conclusion let me say that, as far as my own experience goes, the use of sodium sulphide answers the purpose to a more perfect degree than any other process. Of course many improvements can be made upon the method of application given above; yet, for a rough but satisfactory method, I have found it sufficiently accurate.

An Experimental Examination of the Circumstances which Determine the Action, inter se, of the Gases in the Lead Chamber.

THIS inquiry was entered into in the hopes of being able to throw some light on the interior economy of the lead chamber, as at present used in the manufacture of sulphuric acid. Although the method ordinarily employed to show the theory of the formation of this acid is a very good one, yet there are numerous points which cannot be shown, and which can only be pointed out by the agency of chemical analysis.

No one has yet attempted to do this minutely; and our knowledge of the phenomena of alkali manufacture is in many respects very much behindhand. Experiments have certainly been made, and great successes have been achieved on all sides, but these have tended more to broad generalizations than to exact chemical facts—to the manufacturing, not to the scientific side of the question. The interior of the lead chamber is comparatively an unknown land to us. Lowthian Bell has lately traced the actions occurring in his blast-

furnace through every stage, from the bottom to the top, in a series of most laborious experiments; but no one has yet done this with the sulphuric acid chamber. I now venture to hope that this very limited attempt to, at least, *commence* such an investigation may be of interest, not only to those engaged in the manufacture, but to those who merely look at it from a scientific point of view.

In observing the theory of the manufacture of sulphuric acid, there were many points which it struck me would well repay a closer examination. It is well known that when sulphurous acid comes into contact with one of the high oxides of nitrogen, it deprives it of its oxygen, provided the contact takes place in the presence of steam. But there are many causes which prevent this action; and it is not an uncommon thing to see this experiment fail.

If the heat of the vessel in which the combination is to take place be too high, or if it be not high enough, the result will be failure. And so in practice; every manufacturer knows how careful he must be in regulating the amount of steam he throws into his chamber, otherwise he finds a great amount of sulphurous acid escaping to the atmosphere, a larger amount of nitrous fumes in the acid from his Gay-Lussac tower, and a smaller yield of vitriol.

It is into the laws which regulate the combination of those gases that I wish to inquire; and I have tried to do so, first, by individual experiment, and then by a

careful examination of the lead chamber in which the action takes place.

On the action of Sulphurous Acid Gas upon Nitric Acid Gas.

Although we are indebted to the labours of Clément, Désormes, Davy, De la Provostaye, and others, for the light which has been thrown upon the theory of this action, so far as it relates to sulphuric acid manufacture, yet I trust I may be excused for bringing forward results which differ in some degree from those of the above-mentioned workers.

It is generally understood at the present day that no action can take place between *dry* sulphurous acid and nitric acid gases when brought together in the same vessel; and in all chemical treatises this fact is distinctly stated. Thus, Miller, in his 'Elements of Chemistry,' speaking of the theory of the manufacture of sulphuric acid, says: "*Direct combination, however, cannot be produced between the two gases* (sulphurous acid and oxygen); *the intervention of a third substance becomes necessary, and if water be presented to them a very gradual process of oxidation occurs.*"

Gmelin, also, in his 'Handbook of Chemistry,' observes: "A dry mixture of two measures of sulphurous acid gas and one measure of oxygen *remains unaltered; but if water be present, a very gradual condensation takes place, and sulphuric acid is produced.*" The results arrived at by different observers may be summed up in

the deduction from the above paragraphs, namely:—*That no action can take place between these two gases without the intervention of water, either in the liquid or gaseous state.*

It was with the intention of inquiring more closely into this that the following experiments were made; and the conclusion I have come to, and which I hope to clearly demonstrate, is the very reverse of that generally received: *that action does take place between the dry gases under certain conditions.*

As I was anxious to have the gases in as similar a condition as possible to those in the lead chamber, the sulphurous acid was made from burning sulphur: the nitric acid being prepared from nitrate of soda by the action of sulphuric acid, whilst the air employed was first carefully dried by passing through sulphuric acid and caustic potash, every care being taken to prevent the presence of even the smallest amount of moisture.

Experiment I.—When dry sulphurous acid and nitric acid gases are brought into contact in a perfectly dry glass vessel, which is then hermetically sealed, there is *apparently* no action; but if this vessel, after being allowed to stand for ten or twelve days, be then opened, and the remaining gases expelled, it is found that a decided, though small, amount of sulphuric acid has been formed over the sides of the glass vessel, and may be seen, on examination with the microscope, in the condition of white crystals, soluble in water, and behaving in all respects as sulphuric acid. There are

many things which will prevent this formation, and which I intend noticing further on, such as temperature, &c. This result is greatly hastened, however, by the addition of *a single drop* of water on the end of a fine platinum wire.

The conclusion one was apt to arrive at was that these crystals were neither more nor less than the ordinary chamber crystals; but I was led to doubt this from various circumstances. In the first place, they seemed to differ from the chamber crystals in *form*, these partaking more of the needle-shaped form of the crystals of sulphuric acid; and also, when exposed to the air, they remained a long time (several days, in fact) without change. This shows they are not the same as the chamber crystals. Again, when they were brought into contact with water, they dissolved without the evolution of nitrous fumes, from which we may fairly conclude that they were crystals of sulphuric anhydride.

I had long been inclined to take a different view of the cause of this action from that generally accepted. It seemed to me in all its phases to resemble the action of a small piece of leaven in a loaf of unleavened bread, or the action of a minute crystal dropped into a supersaturated solution of a salt, which immediately causes the solidification of the whole liquid. The action only requires to be commenced, and it then continues till the whole of the attainable oxygen has been made use of. This action, if quickened at all, is only slightly so, by the further addition of steam.

Experiment II.—If, again, instead of inserting a drop of water into the vessel in which the gases are confined, it be surrounded with a coating of ice, the same effect takes place, a much longer time, however, being required.

Experiment III.—The same end can be attained by the *sudden* application of heat.

These results then led me to judge of the action as I have said, showing that the sulphurous acid is able to deprive the nitric acid of *some of* its oxygen without the intervention of steam, a medium which has hitherto been considered necessary.

It has been shown that a very small amount of water can cause the action to commence. The next experiment tried was to find what effect water present in a large quantity had upon the formation of the acid.

Experiment IV.—A mixture of two volumes of steam to one of the mixed gases was put into a glass vessel and allowed to stand twenty-four hours (the gases being mixed in requisite proportion).

Experiment V.—The same amount of the mixed gases was passed into a similar vessel, but into which *no air* was allowed to enter, to see if any action could take place in its absence; and the water was presented to the gases in a liquid condition, and allowed to stand the same length of time. At the end of the time the results were—

	Acid produced calculated to percentage.
Experiment IV. . . .	66 per cent.
Experiment V. . . .	93 „

A certain amount of nitric acid still remaining untouched In both cases, however, the result, in appearance, was a complete combination. Still, on examination, a large amount of nitric acid was found in solution in No. 1 (*Experiment* IV.).

Experiment VI.—Equal volumes of steam and mixed gases were then tried, and the result on examination gave—

	Acid produced calculated to percentage.
Experiment VI. . . .	74 per cent.

From these experiments, then, I considered myself justified in adopting the theory of the leavening nature of the action taking place.

It is also evident that the volume of steam introduced should be less than the combined volumes of the two gases. But let us take another case. Suppose the temperature of the vessel in which the experiment is to take place be raised to 100° C., or kept in boiling water, the results are found to differ in every case.

Experiments VII., VIII., IX.—Taking the same volumes as above, but at the increased temperature, I find the different yields of acid to be thus :—

Experiment.	Acid produced calculated to percentage.	Experiment above.
VII.	86·7	IV.
VIII.	24·5	V.
IX.	80·2	VI.

Here then is quite another phase opened up to us: temperature has a great deal to do with the action

taking place; and as the result of many experiments, I find that its influence may be embodied in the general rule, that "*The higher the temperature the more steam required.*"

The foregoing results thus show the action occurring where nitric acid gas is brought into contact with sulphurous acid gas, both with and without the presence of steam. The next question to be solved is—In what part of the vessel does most action take place?

Most persons who have attended chemical lectures are familiar with the method employed to illustrate the formation of sulphuric acid. The mixture of sulphurous and nitric acids is brought together in a large globe, and steam is then introduced. Ruddy fumes are first formed; then a crystalline deposit takes place, and soon the atmosphere in the globe becomes colourless. But on close examination another peculiarity is seen in the vessel; and that is, that near to the deposit, and long after the ruddiness has disappeared, a very small narrow band of red fumes is noticed wherever the crystallization has taken place. This, then, led to the question being asked—Does not a greater formation of acid take place when some acid previously formed is present? And this question was attempted to be answered by the following experiment:—

Experiment X.—A layer of sulphuric acid from which all moisture had been expelled by long boiling, and which had been previously carefully weighed, was laid in the bottom of the vessel, and the gases allowed to

enter, steam being excluded. The gas at the upper part of the vessel became almost immediately nearly colourless; but a strong and long-continued action seemed to be taking place at the bottom, near the surface of the sulphuric acid, no apparent action being noticed towards the top. On examination no sulphurous acid was found, whilst the weight of acid originally present had increased. (In this experiment, as in the former, the vessel was allowed to stand twenty-four hours.) This seemed to answer the question, especially as upon many repetitions the same results were obtained.

I felt these perfectly satisfactory as laboratory experiments. Some had now to be attempted on a large scale; and through the kindness of an acid manufacturer, I was enabled to make the desired trials; but as in every case I sustained signal defeat, being neither able to cool the chamber sufficiently nor raise it to the required temperature, I found I must, after many disappointments, rest satisfied (as many have found themselves obliged to do) with a knowledge of the fact that what appears perfect in the laboratory will not bear the crucial test of manufacture.

I still felt I had proved the drawback to this to be want of control over the unwieldiness of the chamber. But one fact came out very strongly—that if I wished a good yield of acid, *the increase of steam must be in proportion to the increase of temperature.*

I shall now proceed from laboratory to manufacturing details.

On the Distribution of Gases in the Lead Chamber.

In the preceding chapter the observation is made, when speaking of the laboratory method of showing the theory of sulphuric acid manufacture, "that near to the deposit, and long after the ruddiness has apparently disappeared, a very small narrow band of red fumes is noticed wherever the crystallization has taken place." This then, when taken into consideration along with Experiment X. in same chapter, tended to lead me to the belief that the greatest amount of condensation takes place at the bottom of the chamber, near the surface of any sulphuric acid which has been already formed, and that the upper portion of the chamber is of use principally as a reservoir for the gases; so that if, instead of having a long *high* chamber, one that was long but was of low height were to be employed, the same purpose would be answered to a greater degree, and the expense of chamber-building greatly reduced. It was with the intention of proving

or disproving the truth of this theory that the following investigation was undertaken. The size of chamber in which the experiments were conducted was about 140 feet in length by 30 high and 25 wide. The gases were introduced at the end of the chamber through an iron pipe 12 feet long by 3½ in diameter—the chamber draught very moderate—steam injected at three points in the side and along with the gases at the end. In order to have a definite plan of proceeding I took specimens of chamber air at every 10 feet along its length, 15 feet from the bottom, and also specimens at the same distances at 3 feet from the bottom, thus having

14 analyses, chamber air, at 15 feet,
and 14 „ „ „ 3 „

the first being in reality a bisection of the chamber along its length.

The gases of which the percentages were obtained were Sulphurous, Sulphuric, and Nitric acids.

Before giving my own results, I should be glad if I could quote those of any other observer; but I am unaware of any work having been done on this subject; so that the following observations may be interesting from their newness.

Sulphurous Acid.

Taking, then, in the first place, sulphurous acid, I will show first its distribution in the chamber, then take the two others in the order given above.

As is naturally expected, the largest amount of sulphurous acid is present at the entrance to the chamber; but dispersion takes place very rapidly indeed, so that each 10 feet makes a decided change in the percentage of acid present.

The amount of sulphurous acid present at a distance of 10 feet from end of chamber is 72 per cent., continuing the same till about 20 feet from entrance. There is then a rapid fall to 46 per cent. at 30 feet, falling rapidly still, till at 40 feet from end the amount only equals 31 to 33 per cent. After this the variations are not so remarkable; the amount of sulphurous acid, however, becomes gradually less and less till its lowest point is reached at 120 feet from entrance, where 13 per cent. is the amount present. These analyses were made at 15 feet from bottom of chamber. On those made at 3 feet from bottom the variations are not so sudden. At 10 feet from entrance the amount present is 3 per cent.; this rises rapidly till at 40 feet from end it attains its maximum, and 29 per cent. of acid. It is now at its highest point; and from this it descends very gradually till at 130 feet it falls to 8 per cent., and near its exit rises to 16 per cent.

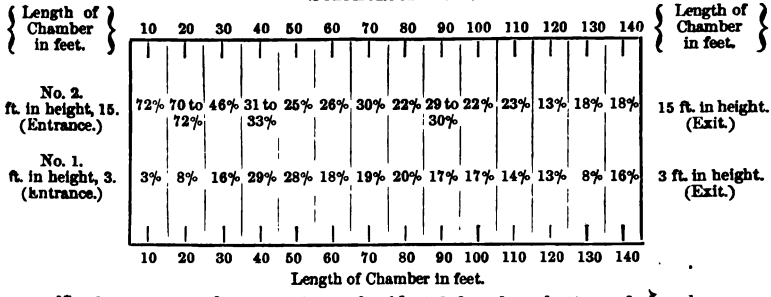
The following diagrams will show the variations more plainly.

DIAGRAM I. (*a*).

(See opposite page.)

DIAGRAM I. (*b*).

SULPHUROUS ACID.



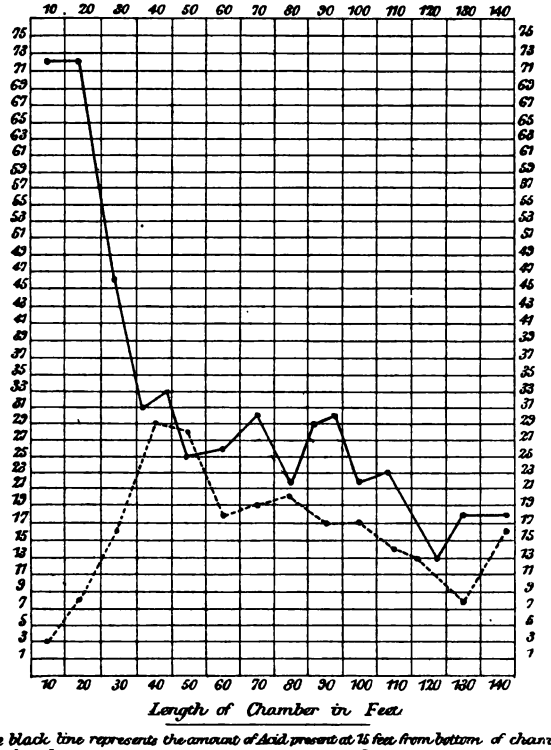
No. 1 represents the percentage of acid at 3 feet from bottom of chamber.
No. 2 " " 15 " "

The figures in the divisions of the above diagram represent the percentages of sulphurous acid corresponding to Diagram I. (*a*), or the numerical variations will be seen more plainly in the following proportional tables:

No. I.—At 15 feet height.		No. II.—At 3 feet height.	
Feet from end of Chamber.	Proportional number.	Feet from end of Chamber.	Proportional number.
120	1	10	1
130, 140	1·4	20, 130	2·6
80, 100	1·7	120	4·3
110	1·8	110	4·6
50	1·9	30, 140	5·3
60	2	90, 100	5·6
70, 90	2·3	60	6
40	2·5	70	6·3
30	3·5	80	6·6
20, 10	5·5	50	9·3
		40	9·6

In looking over Diagram I. (*a*), it may be noticed that

ACID DIAGRAM Nº I. (a).



The black line represents the amount of Acid present at 15 feet from bottom of chamber.
The dotted " " " " " " " " 3 " " " " "

there are three distinct falls in the percentage of acid, and after each there is again a slight rise. It may be interesting to remark, that almost exactly at those parts were the points at which steam was thrown into the chamber. The falls are at 20 feet, 70 feet, and 110 feet respectively, steam being injected at 20 feet, 65 feet, and 110 feet.

The tremendous fall occurring from 20 feet to 40 feet may be accounted for by the great amount of steam entering the chamber at this point, as not only was it entering at 20 feet, but also, along with the gases, at a little below the large iron pipe at the end of the chamber; so that the steam absorbs a large amount of the hot sulphurous acid.

In the analyses at 3 feet these falls are not so noticeable, are indeed not so great, the acid here being out of the immediate action of the steam. In these experiments the temperature of the chamber was kept as low as possible, and the amount of steam allowed to enter the chamber was, as far as could be determined, almost one quarter of the mixed gases. This, then, tends so far to show what I previously imagined, that the upper portion of the chamber was of use principally as a reservoir for the sulphurous acid, allowing it to descend as it was required to the lower, or working portion. This was also tried in another way.

The ordinary funnel-shaped collector usually placed in the chamber, and which communicates with a small leaden jar on the outside, by which a manufacturer

gets an idea of the strength and make of his acid, was brought into use. Instead of being, as usual, placed about 8 feet from the bottom of the chamber, it was in this case placed about 16 feet high, and the amount of sulphuric acid formed was carefully observed.

In this case, after standing nine days, only $\frac{1}{16}$ of an inch of acid had formed, whilst at the height of 4 feet the make of acid was regular and fairly large.

In the former case (at 16 feet) sulphurous acid was continually escaping, whilst the amount in the latter was merely trifling. This, then, was a very fair proof of the truth of my theory.

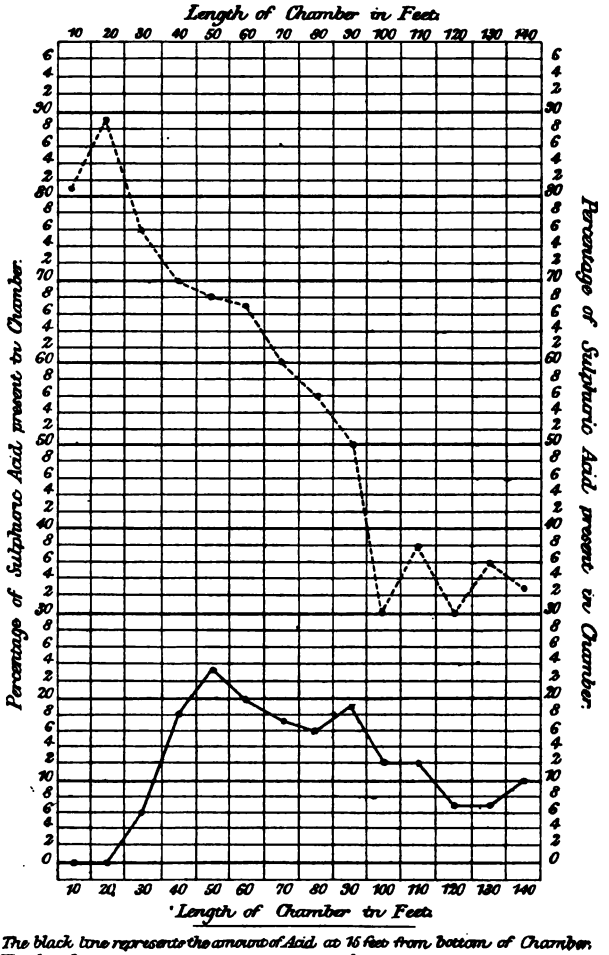
Sulphuric Acid.

Passing from the sulphurous to the sulphuric acid, I find the diagram of percentage in the latter a very strange one. At 10 feet from the point of entrance, where 0 is the percentage of acid to 140 feet, the variation at 15 feet in height is very trifling. The highest amount is reached at 50 feet, showing there only 23 per cent. But at 3 feet in height the analyses present a more extraordinary difference than that of Diagram I.

Beginning again at 10 feet from entrance, I find the amount of acid to be equal to 81 per cent.; then a sudden rise brings it to 89 per cent.; this being the maximum: then comes a most rapid and continuous fall, till at 100 feet the amount is 30 per cent., and remains nearly at this to the end of the chamber.

The following diagrams will show the variations:

ACID DIAGRAM Nº II. (a).



The black line represents the amount of Acid at 16 feet from bottom of Chamber.
The dotted " " " " " " " 3 " " " " "

DIAGRAM II. (*b*).

SULPHURIC ACID.

Length of Chamber in feet.	10	20	30	40	50	60	70	80	90	100	110	120	130	140	Length of Chamber in feet.
No. 2. ft. in height, 15. (Entrance.)	0%	0%	6%	18%	23%	20%	18%	16%	19%	12%	12%	7%	7%	10%	15 ft. in height. (Exit.)
No. 1. ft. in height, 3. (Entrance.)	81%	89%	76%	70%	68%	67%	60%	56%	48%	30%	38%	30%	36%	33%	3 ft. in height. (Exit.)
	10	20	30	40	50	60	70	80	90	100	110	120	130	140	

Length of Chamber in feet.

No. 1 represents the percentage of acid at 3 feet from bottom of chamber.
No. 2 " " 15 " "

The figures in the divisions of the above diagram represent the percentages of sulphuric acid, corresponding to the lines in Diagram II. (*a*).

On comparing this with Diagram I. (*a*), the similarity is very striking. It is only required to place the black line in Diagram I. (*a*) on the red line in Diagram II. (*a*), and *vice versâ*. In No. I. the greatest amount of sulphurous acid is at the top of the chamber, and the smallest at the bottom. In No. II. the largest amount of sulphuric acid is at the bottom of the chamber, whilst the smallest amount is at the top.

PROPORTIONAL TABLES FOR DIAGRAMS II. (*a* and *b*).

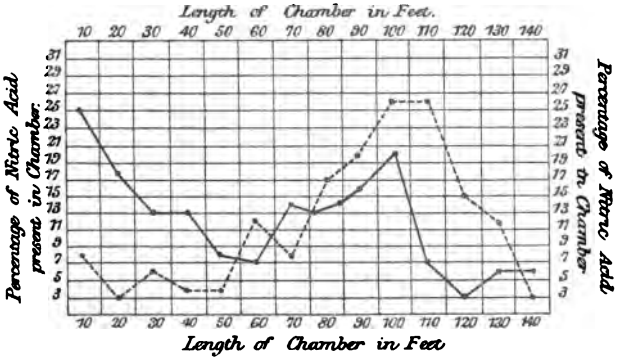
No. I.—At 15 feet height. Feet from end of Chamber.	Proportional Number.	No. II.—At 3 feet height. Feet from end of Chamber.	Proportional Number.
30	1	100, 120	1
120, 130	1·2	140	1·1
140	1·7	110, 130	1·2
100, 110	2	90	1·6
80	2·7	80	1·8
40, 70	3	70	2
90	3·2	60, 50	2·2
60	3·3	40	2·3
50	3·7	30	2·5
10, 20	0	10	2·7
		20	2·9

NITRIC ACID.

The variations in the percentage of nitric acid are not very great, being only between 3 per cent. and 26 per cent., these being the maximum and minimum amounts. It attains its greatest height at 100 and 110 feet from end of chamber, and then sinks very rapidly down to 3 per cent. at 140 feet.

In the following diagrams the figures and lines are similar to those in the preceding.

ACID DIAGRAM Nº III (a).



The black line represents the amount of Acid at 15 feet from bottom of Chamber
The dotted " " " " " " " 3 " " " " "

DIAGRAM III. (*b*).

NITRIC ACID.

Length of Chamber in feet.	10	20	30	40	50	60	70	80	90	100	110	120	130	140	Length of Chamber in feet.
No. 2. ft. in height, 15. (Entrance.)	25%	18%	13%	13%	8%	7%	14%	13 to 14%	16%	20%	7%	3%	6%	6%	15 ft. in height. (Exit.)
No. 1. n height, 3. (Entrance.)	8%	3%	6%	4%	4%	12%	8%	17%	20%	26%	26%	15%	12%	3%	3 ft. in height. (Exit.)
	10	20	30	40	50	60	70	80	90	100	110	120	130	140	

Length of Chamber in feet.

No. 1 represents the percentage of acid at 3 feet from bottom of chamber.
No. 2 " " 15 " "

The figures in the divisions of the above diagram represent the percentages of nitric acid, corresponding to the lines in Diagram III. (*a*).

I also give the following proportional tables for Diagrams III. (*a* and *b*):

No. I.—At 15 feet height. Feet from end of Chamber.	Proportional number.	No. II.—At 3 feet height. Feet from end of Chamber.	Proportional number.
120	1	20, 140	1
130, 140	2	40, 50	1·3
60, 110	2·3	30	2
50	2·7	10, 70	2·7
30, 40	4·3	60, 130	4
70, 80	4·7	120	5
90	5·3	80	5·7
20	6	90	6·5
100	6·7	100, 110	8·7
10	8·3		

We have now gained some results which will enable us to come to some conclusion regarding the most useful form of chamber.

We have seen that the chamber must be divided into two parts—the working portion, and the reservoir (so to speak) for the gases. If, then, instead of employing this reservoir, we lowered the height of the chamber and extended its length, we should have a greater condensing surface, as we have seen that the greater amount of acid condenses near the surface of already-formed sulphuric acid. We should also have a form of chamber better adapted for getting a good draught. It would not be at all difficult for manufacturers to have a table drawn up for the chamber-manager, showing him the amounts of steam necessary to be thrown into the chamber, according to the increase or diminution of temperature; they would thus have a great saving both in the amount of gas escaping useless to the chimney, and also a greater amount of acid manufactured. I shall now proceed to show the temperature at which the greatest amount of action takes place between the gases in the chamber, but would merely mention that it is of the greatest consequence to the manufacturer to take particular notice of the temperatures of his chamber, as upon the successful management of this depends, in a very great degree, the yield of acid, and also that trouble to all manufacturers, the flowering of the sulphur in the acid. This question is entered into more particularly on page 71.

On the Temperature at which Nitric Acid acts upon Sulphurous Acid.

In the previous part of this book I gave one or two laboratory experiments showing some of the conditions under which these gases act upon each other. I now wish to show the temperature at which this action takes place. These experiments were made in a similar manner to the former. I took the glass globe formerly used, and into this the mixed gases were led with the addition of a little water; it was then placed in another vessel containing cold water, arranged so that it could be raised to any required temperature, or boiled if necessary. A thermometer communicated with the interior, its bulb being nearly in contact with the water at the bottom of the globe. The temperature also of the exterior water was accurately observed. At the commencement of the experiment the temperatures were:

Experiment I.

	Fahrenheit.
Interior of globe	36°·7
Exterior water	40°·3

The interior being thus a little cooler than the exterior. The water was now cautiously and slowly heated, the temperature being observed from time to time, whilst the first formation of acid in the vessel was carefully noted, the results being:

EXPERIMENT II.

Minutes.	Outside water. (Fahrenheit.)	Inside globe. (Fahrenheit.)	Remarks.
Commencement	40°·3	36°·7	No action, ruddy fumes.
2	62°·4	39°	" "
4	127°·6	122°·8	Ruddy fumes begin to disappear.
6	154°·3	200°·2	Remarkably quick and energetic action.

The globe was now withdrawn from the hot water in which it was, and again plunged in cold; the temperature soon fell to 81°·5 Fahr., but no change took place in the action, that continuing as active as ever. After it had been left in the water some time it was seen that the great fall in temperature was only temporary; it soon began to rise.

EXPERIMENT III.

Minutes.	Outside water. (Fahrenheit.)	Inside globe. (Fahrenheit.)
Commencement	45°·6	81°·5
2	45°·6	92°·3
6	45°·9	96°·6

At which temperature it remained till the end of the experiment. I find, then, from this experiment that at 200° Fahr. action commences; that at that temperature the sulphurous begins to act upon the nitric acid;

whilst the second experiment shows that the heat developed by the action itself is pretty considerable.

The globe was now left for twenty-four hours in the cold water (see Experiment II.), and after that time had elapsed the contents were submitted to analysis. I here give the results of three analyses:

	Per cent.
Sulphurous acid	6·21
Nitric acid	—
Sulphuric acid	93·91
	100·12

The temperatures at time of this analysis being:

	Fahrenheit.
Inside globe	46°·9
Outside water	47°·3

In the above experiments it is seen that the temperature never rose to the point of boiling-water, but that degree was very nearly approached.

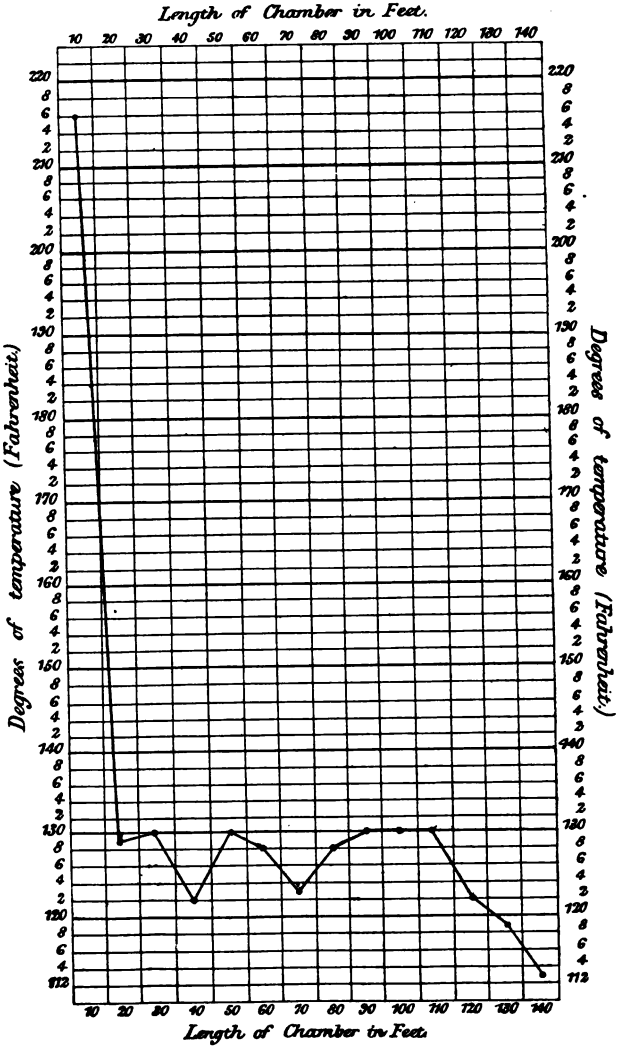
On the Distribution of Heat in the Lead Chamber.

I HAVE shown in the preceding pages that 200° Fahr. is the temperature at which nitric acid begins to act upon sulphurous acid. I now wish to show the temperature of the lead chamber in which the preceding action takes place on a large scale, and then to see if I can draw some conclusion as to the best temperature at which to keep the sulphuric acid chamber.

In order to obtain a good idea of the temperature, I took daily observations at different points in the chamber during a year, and have condensed the results obtained into the form of diagrams.

Ordinary maximum and minimum thermometers were employed, but instead of being fixed as usual upon a wooden back, a *glass* back was employed upon which the degrees were etched, and the thermometers fixed thereto by thick platinum wire, thus having instruments capable of resisting the acid with which they would come in contact. The thermometers were lowered into

HEAT DIAGRAM No. I.



the chamber at the different points by long "threads" of lead, and allowed to remain for about two hours, the yield of vitriol and general appearance of the acid being carefully noted each day. The results obtained by this investigation have been completely borne out by those already shown on pages 47, &c., which, although I considered their proper place in the book to be before the present subject, nevertheless came later in the course of investigation.

As in a former case, I divided the chamber into separate parts, so that I could have some definite plan of procedure. In this case the chamber was divided along its length at four heights, thus:

1st	at the height of	24	feet from	bottom of	chamber.
2nd	"	15	"	"	"
3rd	"	8	"	"	"
4th	"	3	"	"	"

the temperature being taken every ten feet along the length at these heights.

DIAGRAM I.

HEAT OF CHAMBER AT 24 FEET FROM BOTTOM

(See opposite page.)

In looking at Diagram I. the first thing that strikes us is the very sudden fall in temperature which takes place in passing from 10 feet from entrance of chamber to 20 feet, there being a fall here of 87° Fahr. After this the temperature is comparatively constant till it reaches 110 feet from entrance, when it again falls continuously

till it reaches 113° Fahr., at which temperature the gas passes from the chamber.

This is that portion of the chamber which I have previously called the "reservoir," and in which very little, if any, action between the gases takes place; and it is worthy of notice that, with the exception of the first ten feet, at no place in this portion does the temperature rise above 130° Fahr. And if we turn to the preceding pages it will be found that in Experiment II. the nearest approach to this temperature is 122°·8 Fahr.; and here the remark is made, "ruddy fumes begin to disappear." Here then is another proof, if another proof were required, that the upper part of the lead chamber is not of use as a condensing "space," but merely as a reservoir for containing the gases, and, *if necessary*, assisting proper mixture.

In this diagram we may see also the points in the chamber at which steam is thrown in. At 40 feet, and at 70 and 110 feet respectively, we have decided falls of temperature, these being very nearly the positions of the steam-pipes.

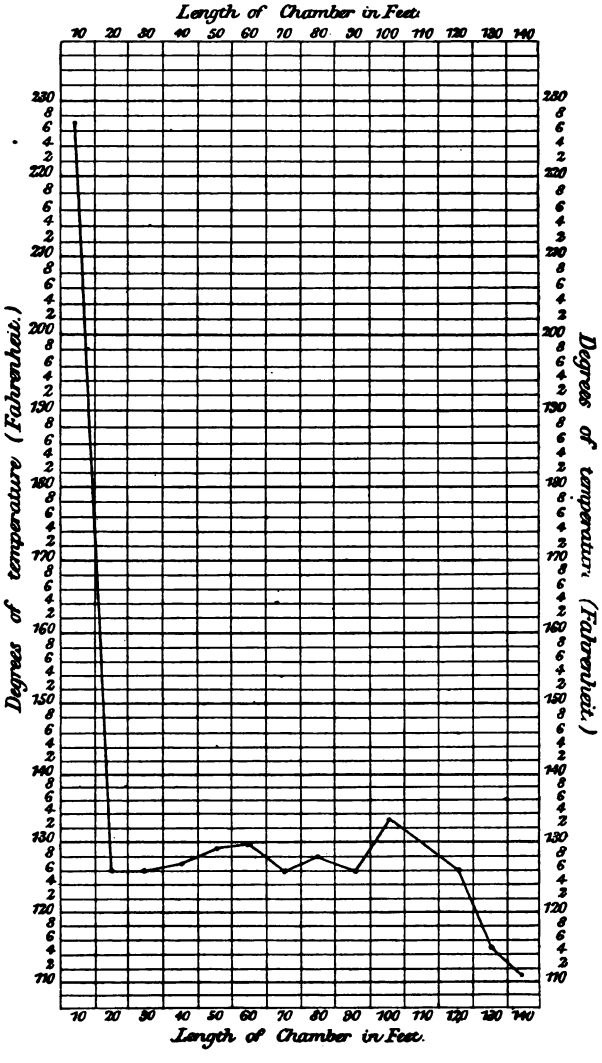
The high temperature at the beginning may be accounted for by the fact that shortly below this the pipe by which the gases are conducted to the chamber is inserted.

DIAGRAM II.

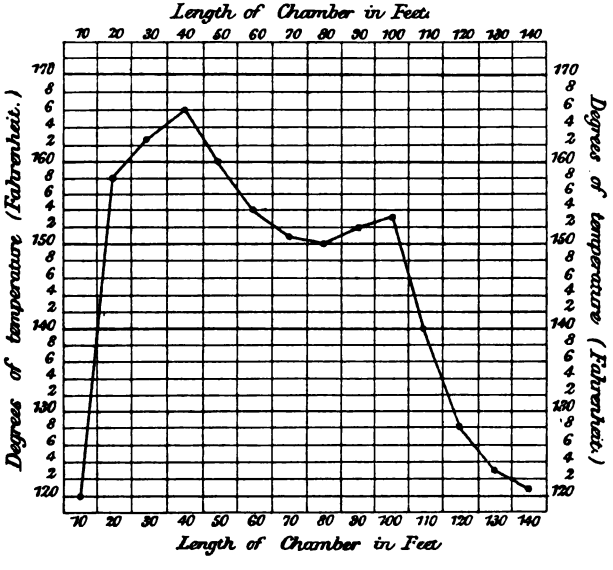
(See opposite page.)

Little is to be said respecting this diagram which has not been said in the former. In this also is noticeable

HEAT DIAGRAM No. II.



HEAT DIAGRAM No. III.



the great fall in temperature which takes place from 10 to 20 feet from entrance to chamber; in this case the fall is even greater than before, changing here from 227° to 126° Fahr.—a difference of 101° Fahr.

This is accounted for by the fact that the entrance pipe is much nearer this point than the former, being in fact just above the spot where the temperature was observed. The regularity of the heat after this sudden fall is also, as in the former case, very remarkable, the variation being between 126° and 133° Fahr. till we reach 120 feet from entrance to chamber, where the temperature falls to 110° Fahr., the average temperature, however, being about 126° to 128° Fahr.; in this case also bearing out the fact (by reference to Experiment II., p. 54) that the upper part of the chamber is unnecessary.

DIAGRAM III.

(See opposite page.)

In Diagram III. I find a higher range of temperature, varying for the most part between 150° and 160° Fahr.; whilst at entrance and exit the temperature is comparatively low, rising towards the centre of the chamber.

Here now we approach very nearly the required temperature, 200° Fahr. being the observed degree at which nitric acid acted on sulphurous acid; this portion of the chamber is really the "working" portion. It is necessary also to observe along with this diagram the next.

DIAGRAM IV.

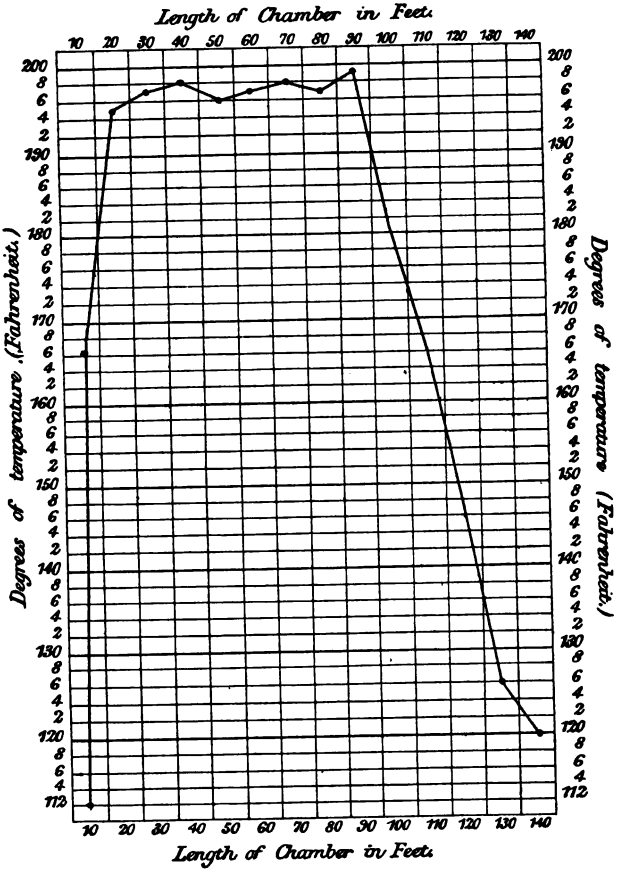
(See opposite page.)

I have already shown experimentally by analyses of the gases at 3 feet from bottom of chamber, that the greatest amount of action went on at that portion; and I have also shown (page 48) that the temperature at which nitric acid began to act on sulphurous acid was 200° Fahr., so that now by observing these two diagrams we shall see how closely the laboratory and the manufacturing results agree. I have already spoken of this in Diagram III., but it is much more distinctly observed in Diagram IV. Beginning at 112° Fahr. the temperature rises suddenly till at 20 feet from entrance it attains 195° Fahr., *whilst the temperature is for the most part from* 195° *to* 199° *Fahr.* After 90 feet from entrance of chamber it falls at an almost regular amount of 20 degrees for each 10 feet of chamber length until at 140 feet from entrance of chamber the temperature is 120° Fahr.

Here then we have the example of almost perfectly suitable temperature. At this time also the yield of vitriol obtained from this chamber was as nearly the theoretical amount as could practically be obtained; and it was found that whenever the temperature of the chamber was allowed to increase or diminish the result was bad.

At this time the amount of nitric acid escaping was almost *nil*, whilst the colour of the liquid coming from

HEAT DIAGRAM No. IV.



the Gay-Lussac tower showed that the gas escaping was NO^2, with a scarcely appreciable amount of nitric acid. (I may here say that whenever the colour of this liquor is of a *dark* red colour it is a sign of the escape either of nitric acid or some of the higher oxides of nitrogen.)

The conclusions I draw from these and the preceding investigations may be summed up thus:—

1. The best form of chamber to be employed is one which is long and not high; the analyses point to one of somewhat the following dimensions—

Length, 150 feet.
Width, 25 or 30 feet.
Height, 10 or 12 feet.

There is thus a large condensing "surface," the mixed gases coming readily in contact with all parts of the chamber, whilst they are also in contact with the previously condensed acid which rests on the sides of the chamber.

2. The temperature of the chamber should be kept as nearly as possible about 200° Fahr.; this fact also acting as a regulator for the amount of steam thrown into the chamber.

3. That in "starting" a chamber sulphuric acid should be run on the bottom in preference to water, as at present generally employed.

An Inquiry into the Best Form of Leaden Chamber.

THE introduction of the leaden chamber into the manufacture of sulphuric acid must be ascribed to Dr. Roebuck, of Birmingham; and the principle of the method employed by him continues as the principle of that in use at the present day.

A mixture of sulphur and nitre mixed in certain proportions was ignited and shut into an *air-tight* lead chamber, the size of which varied from 6 to 10 feet in diameter; after a certain time had elapsed—supposed to have been sufficient to have condensed all the acid formed by the burning sulphur—the chamber was opened, the stand and vessel in which the mixed substances were placed was withdrawn, refilled with the mixture, and again inserted into the chamber, the door of which was then luted on air-tight, as before. This, then, was the rough-and-ready manner in which sulphuric acid was manufactured in this country in the days of the *first lead chambers.* This was the small cloud rising in the horizon which we, in our day, look back upon with a mixture of amusement and wonder.

Once a beginning was made, it was easy enough to proceed, and the first step had been taken.

The obvious disadvantage in this plan was the discontinuity of the process. Each time the chamber was opened the residual gases—those which had not undergone condensation—escaped, whilst the chamber was lying idle till a fresh charge was introduced. This difficulty was overcome by the substituting for the small vessels which were being continually inserted and withdrawn, larger boilers in which the sulphur was burned, thus sending a continuous stream of sulphurous acid into the chamber; then came the introduction of steam by Kestner; and by slow degrees the great manufacture which at the present day contributes so much to the great wealth of England, sprung up.

This chamber, then, is the point upon which the attention is, naturally, most concentrated. In this all the actions take place, and the nature of the work it performs, and the manner in which it performs it, are very imperfectly understood.

In the preceding pages I have shown, although imperfectly, the conditions under which this chamber does its best work; and I now intend, in a very brief manner, to inquire into the best form of chamber, which, it seems to me, is indicated by the preceding observations.

By referring to pages 34–37 it will be seen that the sulphurous acid, after entering the chamber at one end, becomes almost immediately acted upon by the steam and nitric acid with which it comes in contact; that

the action between the gases is very trifling towards the top of the chamber, the greatest amount of action being at the bottom. This leads me to the conclusion that the upper portion of the chamber acts merely as a reservoir for the gases, which it supplies, as they are wanted, to the lower portions, where the conditions are more favourable to the formation of acid.

If, now, instead of using the chambers as at present employed, the height were to be lessened, there would then be a much greater condensing surface than in the present form. And here I should just like to say a word respecting condensing surface. It seems to be tacitly admitted among the greater proportion of sulphuric acid manufacturers that the one thing needful for complete condensation is "condensing *space*;" and "condensing space" and "condensing surface" are often, indeed generally, used as synonymous terms. I have shown that very little, if any, action takes place when there is no "surface;" the presence of some tangible substance seems to influence in some indirect way the action of the gases upon each other. This also seems to be the common-sense view to take; but even among thoroughly practical men the confusion regarding "space" and "surface" seems to be very great.

To return, however, to my subject. Suppose the height of the chamber were diminished, the condensing surface is increased, and there is nothing admitted into the chamber which would tend to baffle the

draught in any way—indeed, according to the shape of the proposed chamber, the draught will be rather increased; we also bring the gases more in contact with any already-formed acid at the bottom of the chamber, which I have shown determines very rapidly the action between the gases. This form of chamber also would be much more easily managed than the one now in use, which, from its very unwieldiness, involves the manufacturer in many expenses which are, in reality, perfectly needless. If, again, the mere item of expense be considered, I think every one will agree that the expense of building a chamber half the size of that in use at present would be a very considerable advantage to the manufacturer. The dimensions of the chamber I would recommend are as follows:—

Length, 160, 200, or even 210 feet.
Width, 30 feet, increasing in ratio to length.
Height, 10 feet, and for any length of chamber the height should not be increased.

I feel confident from my own experience, encouraged greatly by my experiments, that the foregoing size of chamber would be much preferable to our present large-sized ones, and would not only give a much larger yield of vitriol from the same expenditure of sulphur, but would, in the mere matter even of chamber room, be of great value to the manufacturer.

Before leaving this part of my subject, I would like to notice two methods of working sulphuric acid

chambers which seem to me to deserve special attention—those of Mr. Ward and Mr. Gossage.

The method proposed by Mr. Ward consists in adding more *condensing surface* to the chamber, by the introduction of glass sheets or tubes, placed horizontally and longitudinally in the chamber upon which the acid condenses. I extract the following description of the plan from Messrs. Richardson and Watts' Technology.*
" Mr. Ward passes the usual mixture of sulphurous and
" nitrous gases first into a mixing chamber formed of
" lead, which may be of much smaller dimensions than
" the leaden chambers generally employed; for example,
" if the burners are of a size to burn 140 cwt. of sulphur
" pyrites in 24 hours, the mixing chamber may be 64
" feet long, 16 feet high, and 20 feet wide. In this
" chamber the gases become mixed, and on the intro-
" duction of steam a portion of the acid is condensed.
" From the mixing chamber the gases remaining un-
" condensed pass into a second chamber, also made of
" lead, and (for burners of the dimensions stated) about
" 200 feet long by 3 feet high, and 3 feet wide; the
" bottom of this chamber should be divided into four
" equal parts, to allow of the acid being run off sepa-
" rately. Within this chamber, sheets of glass are
" arranged horizontally and parallel to one another,
" at a distance of about an inch apart. The sheets of
" glass are supported, one over the other, on strips of

* Richardson and Watts' Technology, Vol. I., Part V., Appendix A, page 198.

" glass or earthenware supports, until the pile reaches
" to the top of the chamber. The sheets may be of
" any convenient length, and each layer is placed end
" to end, until the layer extends to a distance of, say,
" 25 feet. The cover of the chamber may be made in
" sections, so that it may be readily removed for con-
" venient access to the glass. The portion of the
" chamber thus filled with the pile of glass is divided
" by it into a series of narrow passages running the
" whole length of the pile, and through them the gases
" are compelled to pass. At the end of the first pile
" a space is left in the chamber, about 4 feet in length,
" to allow the gases again to mix freely, and then
" another pile of glass similar to the first is formed,
" and in this way the chamber is filled, the piles of
" glass and mixing spaces occurring alternately at
" equal distances apart. Steam is introduced into the
" second chamber at the end next to the first chamber,
" and in sufficient quantity to produce acid of from
" 1·675 to 1·750 specific gravity in the farthest or last
" division of the second chamber. This acid contains
" a considerable quantity of nitrous acid and nitric
" oxide; it is run back into the leaden trough leading
" from the burners to the first chamber, where, by the
" action of the sulphurous gas and steam, it is deprived
" of its nitrous acid and nitric oxide. Glass tubes of
" about an inch in diameter may be employed instead
" of the sheets, the tubes being laid horizontally and
" longitudinally within the chamber, so as to produce a

" similar range of piles. The glass employed should " contain as little alkali as possible, otherwise it will be " slowly acted on by the acid. If the draught through " the chimney to the chambers is weak, so that it would " be less injuriously checked by these arrangements, the " sheets of glass may be placed at greater distances " apart; or if tubes be employed, they may be made " larger in diameter; the greater the extent of surface, " however, introduced into the chamber, the greater is " the advantage obtained, so long as the draught is not " injuriously checked, the exposed surfaces tending to " accelerate the chemical changes and facilitate the " condensation of the acid. The quantity of steam " introduced into the second chamber should be carefully " regulated within the limits stated, as, if less be in- " troduced, the acid will be liable to form, in cold " weather, a crystalline mass filling up the passages " and retarding the draught; and if the quantity of " steam is largely increased, the quantity of acid " obtained from a given quantity of pyrites will be less, " and a loss of nitrous acid and nitric oxide will also " result.

" The patentee adds that the following advantages " are gained by this plan:—A greater quantity of acid " may be manufactured in a given space; a greater " quantity of acid may be manufactured from a given " quantity of pyrites or sulphur; a much smaller " quantity of nitrate of soda is required, and the wear " and tear of the chambers is reduced."

Before making any remarks on Mr. Ward's process I shall refer to that of Mr. Gossage.

Mr. Gossage's specification, dated A.D. 1857, January 13th, No. 107, treats of "Improvements in the manufacture of sulphuric acid, and in the construction of apparatus used for such manufacture." The only part of this patent I intend touching upon is that connected with the form of chamber Mr. Gossage proposes to employ. In this specification he says the first thing is, "The construction of chambers to be used in the "manufacture of sulphuric acid, of which the height "is greater than the horizontal length, and through "which gases employed for the manufacture of sulphuric "acid are caused to pass in a vertical or nearly vertical "direction."

In these two patents we have what seems to me a step in the right direction, but a step which few, if any, have taken. Here we see a striving after condensing *surface*, and not condensing *space*. It is well known that condensation takes place more rapidly near the *surface* of a vessel than near the middle, but in many patents this fact seems to have been disregarded.

A great cry used to be for a large chamber—one with *plenty of room in it*—this was the idea of one of our greatest manufacturers; whereas the idea embodied in Mr. Ward's patent is much nearer the truth, although it is not quite it; at least, it seems to me we have in it a perplexity of means to attain a simple end. Mr. Ward has first a small *mixing chamber* into which the

gases pass before entering the large chamber, when the greatest amount of condensation takes place. Again, the presence of the glass tubes in such large quantity may serve, as Mr. Ward himself says, to baffle the draught. What goes on in Mr. Ward's *two* chambers is exactly similar to that occurring in the *one* chamber in general use in sulphuric acid manufacture, with the difference that Mr. Ward gives additional condensing surface. But the chamber in which the glass tubes are placed (which after this I will call the second chamber) must be proportional in size to the amount of sulphur admitted to the chamber, so that if he had fewer kilns he would require to curtail the *length* of the second chamber and most probably the *capacity* of the first—that is to say, he would simply have less condensing surface. (I say the *length* of the second chamber, as I do not for a moment imagine he would further baffle the draught by diminishing *the height or width.*) Here, then, it appears to me we have rather a useless expenditure of appliance. If Mr. Ward did away with the interior padding of his second chamber, and raised its height, say, to 8 or 10 feet, with a corresponding difference in width, still, however, keeping the same length, he would have, for an average amount of acid, obtained a less expensive chamber, and one which would be quite as efficient for the required purpose. I have shown in a preceding page that in the ordinary chamber the greatest amount of action between the gases takes place at the bottom of the

chamber, whilst little or no action takes place above; if then the chamber be extended in length, and diminished in height and width, the required purpose is answered. Let the draught be only moderately fast, and from one chamber pass the gases into another similarly constructed (as is done now with the present form), and we have a very inexpensive chamber; in fact, we have the greatest amount of work done with least outlay. This is evidently the principle of Mr. Gossage's chamber, only he recommends a vertical instead of a horizontal passage of the gases. There is one great drawback, however, in this process; he does not allow the gases to be exposed to the surface on which they condense most readily—I mean the surface of already-formed sulphuric acid. I have already shown that the action between the gases takes place much more rapidly when sulphuric acid is already present in the vessel; and this is a fact well known to some manufacturers; but if Mr. Gossage's chambers were to be laid horizontally instead of vertically, there would be a greater exposure to this surface, and therefore a greater yield of acid, and would also be the form of chamber which Mr. Ward recommends, minus the padding, and the one which I have already said seems to be distinctly pointed out by chemical analysis and careful investigation of the various conditions under which the maximum amount of sulphuric acid is formed.

On the "Gay-Lussac" Tower, and Escape of Sulphurous Acid to the Atmosphere.

In the preceding pages I have entered minutely into the chemistry of the actions which take place in the lead chamber. I must now pass from the particular to the general. The first thing which attracts attention after the actions which take place in the chamber is the escape of sulphurous acid to the atmosphere.

Although the principle involved in the "Gay-Lussac" tower is very perfect, there are many practical difficulties in the way. In the first place, the strength of the acid which is being pumped up to the top of the tower should be of a strength of about 1°·75 Twaddell. It is difficult to be always sure of this. Workmen are very apt to neglect this part of the precautions, and to use the first acid that comes to hand; and it is very frequently found that the acid being pumped up is the ordinary chamber vitriol of 1°·5 Twaddell, or perhaps a little stronger, having been exposed only a very short time to the heat of the evaporating pans. Then, again, the chamber draught requires to be very carefully regu-

lated, otherwise a large amount of the nitrous fumes escapes the sulphuric acid in the tower and makes its way to the atmosphere; upon this draught depends also, as I have shown, the amount of sulphur which must be burned in the kilns.

These are only one or two of the difficulties which prevent the complete action of the principle, perfect theoretically, of the Gay-Lussac tower. Again there arises the difficulty of finding the requisite supply of nitric acid. It is, I may say, impossible to have the theoretical amount of nitric acid present which is required to convert the total amount of sulphur being burnt, so that manufacturers have to choose between two evils—either allowing sulphurous or nitric acid to escape; and, as practical men, they give in their adhesion to the principle of losing that which costs least; so that less than the requisite amount of nitric acid is added, while a very considerable amount of sulphurous acid gas escapes to the atmosphere.

There have been some plans proposed which would in reality do away with the Gay-Lussac tower altogether, but these are, when inquired into, seen to be merely modifications of that plan. Of these, the most important, to my idea, was one brought forward some years ago by Mr. Hofmann, and which was tried in this country, with very indifferent success, by Mr. Peter Spence, the great alum manufacturer.

In the 'Berichte der Deutschen Chemischen Gesellschaft zu Berlin,' No. 1, 1870, Mr. A. W. Hofmann pro-

poses a new method of working the chambers used in sulphuric acid manufacture. His plan is based upon the generally accepted idea that the use of the nitric acid is to act as a carrier of oxygen from the air to the sulphurous acid. Theoretically, therefore, a given amount of nitric acid ought to be able to convert an unlimited amount of sulphurous into sulphuric acid, provided air was present in a large enough quantity and that there should be absolutely no loss of nitric acid. That this is not the case every manufacturer knows, and therefore Mr. Hofmann endeavours to discover the reason why, even when the chambers are worked properly, there is a loss of nitric acid. Although Mr. Hofmann has not got to the bottom of the question, yet his results are very interesting:—

"When sulphurous acid is caused to pass into nitric acid which contains some sulphuric acid (sp. gr. 1·676 to 1·714), the nitric acid is converted into compounds which form along with the sulphuric acid present the so-called chamber crystals, without any perceptible formation of protoxide of nitrogen; but when the nitric acid is impregnated with a sulphuric acid (sp. gr. 1·532), and the experiment just alluded to repeated, there is formed a considerable quantity of nitrogen, which is, of course, quite as injurious to the process as the presence and formation of protoxide of nitrogen. The explanation of this phenomenon is the insufficient strength of the sulphuric acid to form in combination with the higher degrees of oxidation of nitrogen the so-called chamber

crystals. This having been ascertained, the author applied his knowledge of these facts in the following manner on the large scale:—The quantity of steam admitted to the first chamber (the so-called tambour) was so regulated as to produce acid only at 60° Beaumé (sp. gr. 1·714 = 143° Twaddell), with the striking result, fully confirming the laboratory experiment, that a far smaller quantity of nitric acid was required for the same production of sulphuric acid. The author adds, that if, by accident, the strength of the acid in the aforesaid chamber should fall below the specific gravity first alluded to, it can be easily brought up to that strength by the addition of acid of 66° Beaumé (sp. gr. 1·847 = 169° Twaddell). By this contrivance it is possible to manufacture sulphuric acid with a consumption of only 1 lb. of nitric acid for 100 lbs. of sulphur burnt." *

A modification of this plan of Hofmann's was used by Mr. Spence, of Manchester, which consisted in the method of manipulating the chambers. Mr. Spence put three chambers in connection with each other. Into chamber No. 1 he passed the sulphurous acid from the kilns, working this chamber in the ordinary manner, getting an acid of specific gravity 1·5. Chambers No. 2 and 3, however, he worked without steam, thus raising the specific gravity of the acid to 1·715. The acid condensed in chambers No. 2 and 3 runs back to chamber No. 1, when the acid of specific gravity 1·715, which contains a considerable quantity of nitric acid, gives

* 'Chemical News,' vol. xxi., p. 106. 1870.

this up on coming into contact with the diluted acid in No. 1, having thus less loss in nitric acid, and thus reducing the amount of nitre required to be used. Mr. Spence gives some numbers which are interesting as regards this method of procedure :—

"When I commenced operations my consumption of nitrate of soda was exactly 4 tons 2 cwt. weekly. I have reduced it down to 3 tons, and my acid is still of good colour, showing sufficient nitric; and last week my production was rather over my average."* Mr. Spence was at this time requiring 90 to 100 tons of acid of specific gravity 1·845 per week. In the same letter he says: "I think I see my way to working with 2 tons nitrate instead of 4 tons 2 cwt."

However, as Mr. Spence himself saw, this was merely a modification of the Gay-Lussac tower, with the exception that no tower was used, but that the two last chambers acted that part, the acid in which absorbed the escaping oxide of nitrogen, and gave it up on coming in contact with the acid in chamber No. 1, which contained a large amount of water.

The principal objection raised to this was the wear and tear the chambers were subjected to by the action of the nitric acid. In the two last chambers the action upon the lead must have been very great, as both the sulphuric and nitric acids must have been acting upon it. I must certainly also agree with Mr. Spence when he says that not only does he not believe in Mr. Hof-

* 'Chemical News,' vol. xxi., p. 189. 1870.

mann's theory,* but that "the theory of sulphuric acid production, as well as the facts of the Gay-Lussac process, in my opinion, disprove Mr. Hofmann's hypothesis."

We have here a very good illustration of the method employed (and which, I might almost safely say, was called into existence by the invention of what is now known as the Gay-Lussac tower) of making an effort to prevent the consequences which are sure to follow a fault instead of attempting to correct the fault itself. In this case, instead of a careful inquiry into the cause of the escape of nitric oxide, we take it as a recognised fact that such a gas *must* escape, and that our only hope rests in some method of absorbing it, whilst the theory upon which the whole superstructure of this manufacture is built tells us plainly and unceasingly that there should be no such escape, and that any escape is owing to our own carelessness. It is not often carelessness brings out great results, yet it has done so most undeniably in this case; but the Gay-Lussac tower once invented, we have fallen back into *more* than our old carelessness.

To proceed now to the second part of this paper—the escape of sulphurous acid to the atmosphere.

In the greater number of chemical works such an escape does take place; in some there are various methods employed to make use of the gas. The most common one is that of passing it over with irite, and thus

* 'Chemical News,' vol. xxi., p. 224. 1870.

getting a sulphate of barium. This plan is really a very good one, but for my own part I find that it interferes a great deal with the draught, and that after all a very large amount of acid escapes.

In an alkali works near Manchester the following amount of sulphurous acid gas was escaping:—

	SO_2 per cubic foot.
June 10, 1872	2·13
June 21, „	3·90
June 22, „	3·66
July 19, „	5·65

Here we have an idea of the great escape of this gas to the atmosphere. I have also been informed by some chemists that in the works with which they are concerned as much as 12 per cent., and even 15 per cent., escapes.

Surely this can be stopped in some way? Parliament has effectually stopped the great escape of hydrochloric acid gas, by the Alkali Act of 1863; and surely the time has come when the escape of this and other noxious gases should be prohibited under heavy penalties. Alkali manufacturers would in reality be gainers by such a law, the amount they lose annually by the present system being extremely large.

Dr. Roscoe, of Manchester, in a 'Report on the State of Chemical Works,' makes 0·25 grain sulphur per cubic foot as an allowance of escape of sulphurous acid from the chimney. This is very moderate; few works will keep within such bounds. If Parliament

were to take up the point and institute investigations regarding it, I am afraid they would have to come to the conclusion that twice that amount would be the maximum escape allowed.

I hope, however, before long to see a very different state of affairs in this manufacture. The residents in the neighbourhood will be very glad to find the escape lowered to 0·5 grain per cubic foot, and I venture to say will not complain greatly of this amount.

I must now conclude. I have brought together in this small volume facts which, scattered though some of them are, and comparatively insignificant, yet are of great value to manufacturers of sulphuric acid. I hope this book may be of real use in helping those who are too much engaged in the merely business part of the work, to be able to see, in the very hurried glance which so many of them get over their works, the particular points to which attention ought to be paid, and to see with their own eyes what they must otherwise take upon the assertion of their foreman or manager.

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